



Photocatalyzed and photosensitized conversion of organic dyes on porous and non-porous air–solid surfaces: Kinetic models reconsidered



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ARTICLE INFO**Article history:**

Received 10 June 2014

Received in revised form

10 September 2014

Accepted 16 September 2014

Available online 23 September 2014

Keywords:

Photocatalyst

Kinetic model

Dye oxidation

ABSTRACT

The use of organic dyes to assay photocatalyst activity in air–solid systems has been explored frequently in recent years. We earlier proposed a two step kinetic model for photocatalyzed conversion of dyes in sub-monolayer and multi-layer deposits on titania films and powders. The present paper reconsiders both our own work and that of other researchers to propose more fundamental kinetic models which include the influence of illumination profiles within porous films and powder layers. The new models are shown to rationalize results for dye–photocatalyst data from multiple laboratories published over the last two decades. This outcome indicates that different kinetic analyses must be used to obtain rate constants in non-porous, uniformly illuminated systems (e.g., self-cleaning glasses) vs. porous systems such as thick macro- and meso-porous layers and powders, which exhibit illumination intensity variation with depth.

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1. Introduction

We showed in 2006 [1] that the near-UV photocatalyzed bleaching of four dyes could be represented as two first order reactions in series:



The resultant kinetic model was reasonably fitted to TiO_2 powder photocatalyzed conversions of sub-monolayer dye deposits of Acid Blue 9 (AB9), Acid Orange 7 (AO7), Reactive Black 5 (RBk5), and Reactive Blue (RB) (Fig. 1). This same kinetic model we later applied successfully to dye multi-layers of AB9 and RBk5 deposited on non-porous Pilkington Activ™ glass [2]. Mills et al. [3] also found this model satisfactory for AO7 conversions on meso-porous titania films, but not for methylene blue (MB), apparently adsorbed as dye aggregate when dried on TiO_2 , and which followed a zero order bleaching after a 5 min initial period.

While the satisfactory fitting of model to data from two labs and on either porous or non-porous systems was encouraging, several

questions arose which have led us to reconsider the model and its assumptions. These questions are:

- (i) Non-porous titania layers convert stearic acid (SA) (octadecanoic acid) [4,6,7] and palmitic acid [5] multi-layers according to zero order kinetics. Why should our dye multi-layers on non-porous Activ™ TiO_2 coated glass exhibit sequential first order behavior [2]?
- (ii) Stearic acid multi-layers on non-porous titania exhibit zero order kinetics [4,6,7], whereas an apparent first order behavior is observed when SA is distributed within porous titanias [7,8]. We developed a model which predicted that an intrinsic zero order reaction would exhibit apparent first order behavior in porous systems due to the variation of irradiance, and thus photocatalyzed rate constant, with depth into the photocatalyst [9]. Do our dye data [1,2] and that of others for dyes distributed throughout a photoactive porous solid display a similar disguise?
- (iii) Outdoor use of dyes as proxies for pollutants deposited on external photocatalysts (self-cleaning glasses, paver stones, etc.) may show dye bleaching on TiO_2 via photosensitization by sub-bandgap solar illumination [11–14]. What are the corresponding kinetics of photosensitized dye conversions? How might this dye degradation pathway complicate assays for photocatalyst activity when using broad spectrum light

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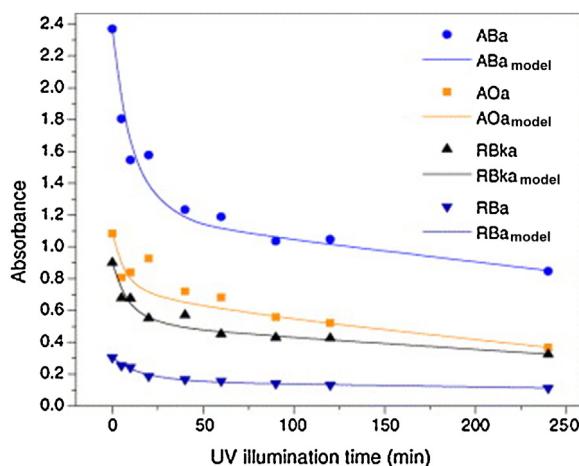


Fig. 1. Series reaction model: Indirect Analysis of ABa, AOa, RBka and RBa [1]. Curves: best fit to first order series model.

sources such as solar (external) or high pressure mercury lamps?

2. Experimental results

All data presented here are taken from the original Refs. [1–8,10–14] which may be consulted for details.

3. Discussion

We first consider a simple model for photoreaction reaction within a porous photocatalyst.

3.1. Reconsideration of model: photocatalytic dye oxidation

Our earlier model [9] for multi-layer stearic acid (SA) photocatalyzed conversion within a porous titania films predicted an apparent first order kinetics (i.e., linearity of $\ln(\text{integrated IR})$ vs. time, even though the intrinsic local kinetics are zero order. We showed that a zero order reaction distributed throughout a porous system with an exponentially decreasing illumination profile, and thus decreasing rate constant, within the layer could be approximated by summing over the successive, differential photoactive layers 1, 2, 3, 4, ... The rate constant of successive layers was taken as one half that of the preceding layer, thus approximating an exponential decline with depth. For this case, in the i th layer, the mass M_i remaining of $-\text{CH}_2-$ groups (IR signal) decreases linearly in time, thus Eqs. (1a)–(1d) apply:

$$M_1 = M - kt \quad (1a)$$

$$M_2 = M - \left(\frac{k}{2}\right)t \quad (1b)$$

$$M_3 = M - \left(\frac{k}{4}\right)t \quad (1c)$$

$$M_4 = M - \left(\frac{k}{8}\right)t \quad (1d)$$

...

This resulting zero order intrinsic model [9] fitted an apparent first order behavior (Fig. 2a and b), in agreement with earlier stearic acid (SA) experimental results of Mills et al. [7] and Allain et al. [8] when using meso-porous titania films rather than non-porous titania [9].

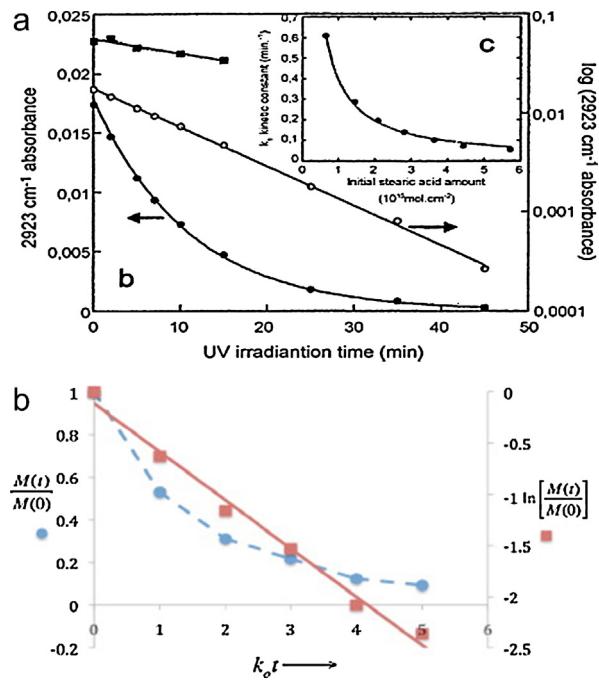


Fig. 2. (a) Removal of stearic acid films from mixed titania–silica photocatalyst layers (Allain et al. [8]; reprinted with permission) (solid circles: absorbance vs. time; open circles: $\log(\text{absorbance})$ vs. time. Inset: apparent first order rate constant vs. initial stearic acid amount). (b) Stearic acid photocatalyzed oxidation in porous titania–silica films. Filled circles: normalized mass ($M(t)/M(0)$) vs. time; filled squares: $\ln(\text{normalized mass})$ vs. time. Linear semilog plot indicates apparent first order reaction (from [9]). Reprinted by permission.

These stearic acid (SA) model results [9] demonstrated neatly the notion that the spatial layer-by-layer variation in irradiance, and thus rate constant and rate, leads to a kinetic disguise of reaction order, shifting the apparent SA kinetics from intrinsic zero order [4,6,7] to first order [7,8].

We now ask if this phenomenon is present in the same geometry, i.e. porous TiO_2 , for our dye- TiO_2 powder layers.

Julson's dye experiments were conducted under sub-monolayer deposition circumstances [1]. Under this dilute, sub-monolayer situation, we may expect an intrinsic first order rate of dye photocatalyzed oxidation. For each dye layer, a simple first order reaction would show remaining original dye mass decreasing exponentially with time:

$$\ln\left(\frac{D}{D_0}\right) = -kt \quad (2a)$$

$$\ln\left(\frac{D_1}{D_{10}}\right) = -\left(\frac{k}{2}\right)t \quad (2b)$$

$$\ln\left(\frac{D_2}{D_{20}}\right) = -\left(\frac{k}{4}\right)t \quad (2c)$$

$$\ln\left(\frac{D_3}{D_{30}}\right) = -\left(\frac{k}{8}\right)t \quad (2d)$$

...

These Eqs. (2a)–(2d) are linear in time (t), as were the earlier Eqs. (1a)–(1d) for zero order reaction. We may expect their sum to again approximate an apparent kinetic order larger by 1 than the intrinsic kinetics. If this expectation is true, we anticipate an

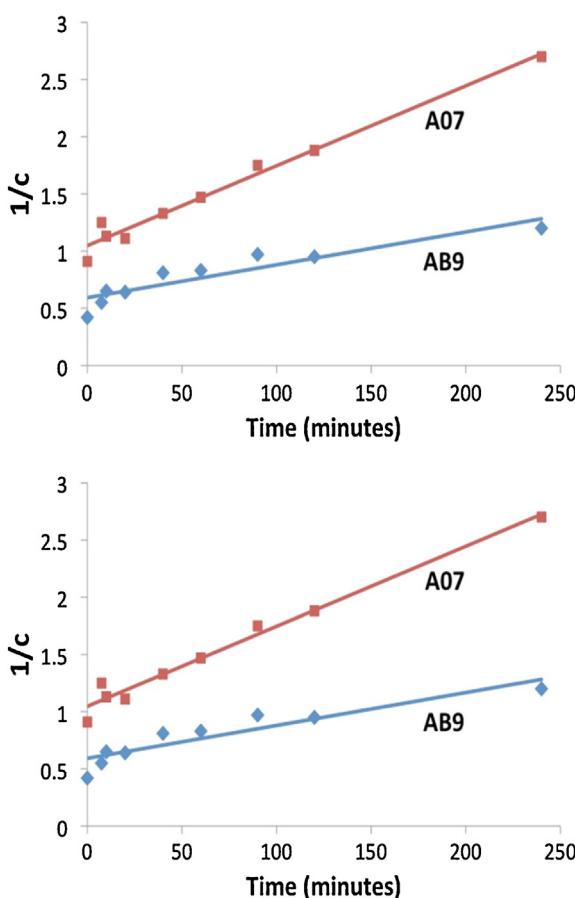


Fig. 3. Original data of Julson and Ollis [1] replotted as reciprocal concentration vs. time for dyes Acid Orange 7 (AO7), Acid Blue 9 (AB9), Reactive Blue 10 (RB19), and Reactive Black 5 (RBk5).

apparent 2nd order behavior in this case. We test this expectation as follows: If a truly second order reaction existed, then in terms of integrated infrared (IR) data for total remaining mass of dye,

$$\frac{dM}{dt} = -kM^2 \quad (3)$$

hence integration would give

$$\frac{1}{M(t)} - \frac{1}{M(0)} = -kt \quad (4)$$

The data for Julson's four dyes [1] in a porous dye-photocatalyst powder aggregates are plotted as $1/M$ vs. t in Fig. 3, which shows a satisfactory fit for three of the four dyes explored. Thus the photocatalyzed oxidation appears to be second order, even though the presumed intrinsic order is first. In this case, the kinetic rate disguise and plots (Fig. 3) are consistent with our recent analysis [9] of SA photocatalyzed oxidation.

To corroborate our assumed intrinsic first order behavior, we consider the photocatalyzed oxidation (PCO) of Rhodamine B (RhB) reported by Wang et al. [10] (Fig. 4). These workers examined optically transparent (30–60 nm) $\text{TiO}_2\text{-SiO}_2$ meso-porous (50–250 nm pore diameters) films, finding apparent first order kinetics for PCO of trace, sub-monolayer dye coverages, as we would expect for an approximately uniform illumination throughout the mixed-oxide layer.

This assumed optical transparency of Wang et al's film is deduced from their data [10]. Plotting the slopes (rate constant) of their four films (Fig. 4) vs. n , the number of dip-coat photocatalyst layers, provides a linear result (Fig. 5), indicating that each additional photocatalyst layer was equally active, i.e., that the local

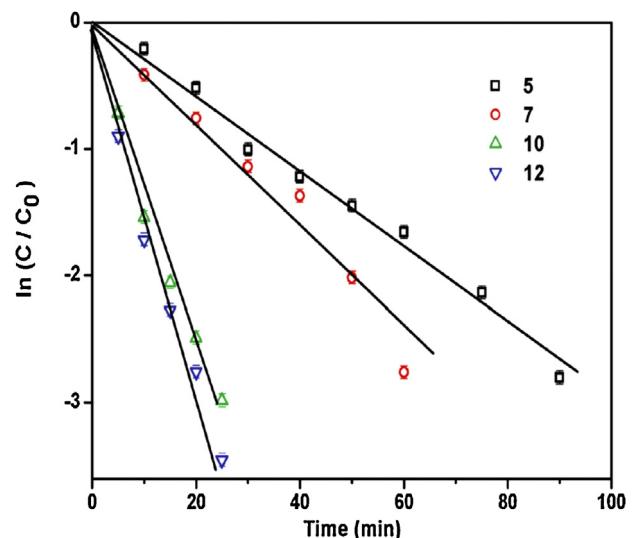


Fig. 4. Semilog plot of concentration vs. time for PCO of Rhodamine B (RhB) in transparent $\text{TiO}_2\text{-SiO}_2$ porous film [10].

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rate constant, and thus light intensity, were approximately uniform throughout their dip-coated films. (Note that the first several layers appear to be nearly photo-inactive, i.e., $k(\text{min}^{-1})$ approaches zero at an extrapolated film thickness of $n = 3.5$ layers. No explanation was offered for this behavior, but one possibility could be sodium diffusion from the underlying glass substrate during dip coated film calcination at 400°C for 3 h, which could have led to inactive early layers.)

Thus the models in this paper correctly predict observation of intrinsic kinetic order for optically transparent films (rate constant independent of depth), and kinetic disguise for optically thick films (rate constant varies with depth) due to non-uniform illumination profiles within the film.

3.2. Extension of model to dye photosensitization by TiO_2

Illumination of TiO_2 with sub-bandgap photons does not provide semi-conductor excitation. However, photosensitization may occur [11a,b], where photoexcitation of the dye molecule is followed by donation of an electron from the dye to the TiO_2 conduction band (Fig. 6) [11a]. If the electron is subsequently scavenged by O_2 ($\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$), then the dye typically is irreversibly bleached, i.e., decolorized. Vinodgopal et al. [12], Nasr et al. [13], and Porade and Gade [14] studied visible light illumination of sub-monolayer dyes adsorbed on TiO_2 (powders, particle films) in air-solid systems. Under these circumstances, photosensitization is

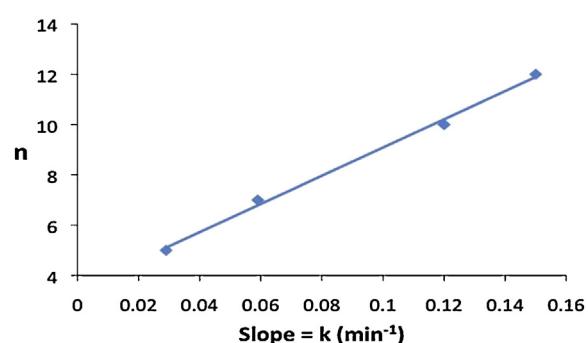
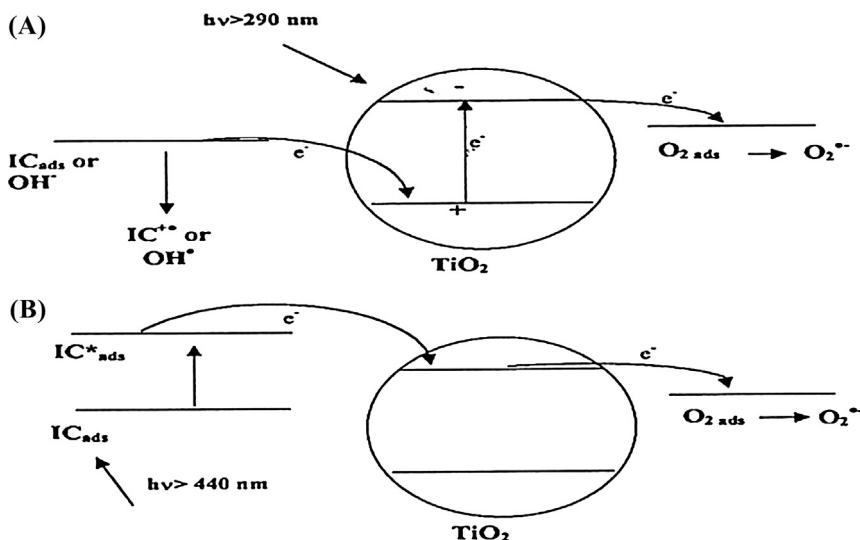
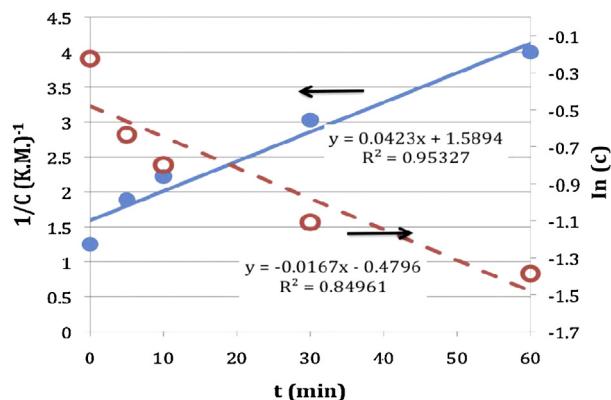


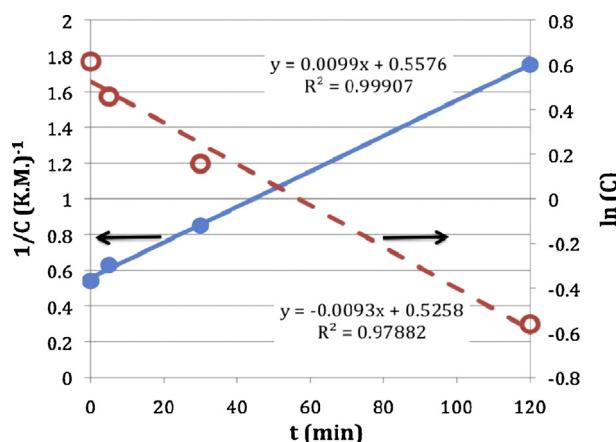
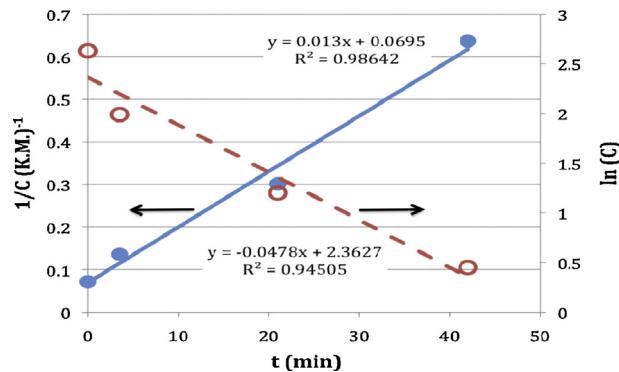
Fig. 5. Number (n) of $\text{TiO}_2\text{-SiO}_2$ deposition layers vs. rate constant (slopes of Fig. 4 lines).

**Fig. 6.** Pathways for photocatalysis (A) vs. photoexcitation (B).

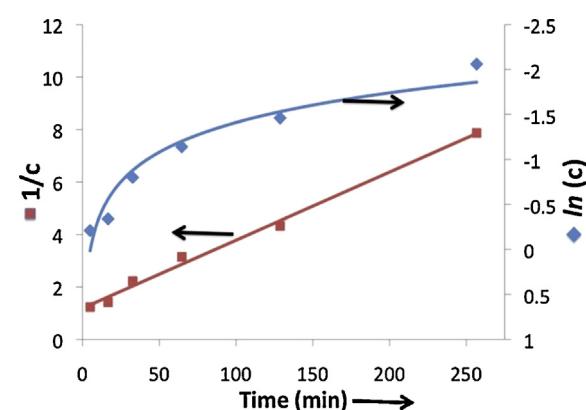
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**Fig. 7.** Data of Vinodgopal et al. [12] (0.02 mol AO7/g) plotted as apparent first order ($\ln(C)$ vs. t) and second order ($1/C$ vs. t) reactions.

intrinsically a first order process. TiO_2 particles do not absorb visible light ($>420 \text{ nm}$), but have a high reflectance [15], giving rise again to an exponential decrease of visible light intensity with depth into the titania porous film or powder. Sol-gel derived films may have much smaller scattering power.

**Fig. 8.** Data of Vinodgopal et al. [12] (0.10 mol AO7/g) plotted as apparent first order ($\ln(C)$ vs. t) and second order ($1/C$ vs. t) reactions.**Fig. 9.** Data of Nasr et al. [13] for dye NBB photosensitized oxidation plotted as apparent first order ($\ln(C)$ vs. t) and second order ($1/C$ vs. t) reactions.

Our analysis of an intrinsic first order process under non-uniform illumination may again be applied. In Figs. 7–10, we compare first order and second order plots of their visible light photosensitized decolorization data, finding in all cases that the second order plot provides fits as good as or better than a first order plot, for the limited data available from laboratory work of Vinodgopal et al. [12], Nasr et al. [13], and Porade and Gade [14].

**Fig. 10.** Data of Porade and Gade [14] for dye photosensitized oxidation as apparent first order ($\ln(C)$ vs. t) and second order ($1/C$ vs. t) reactions.

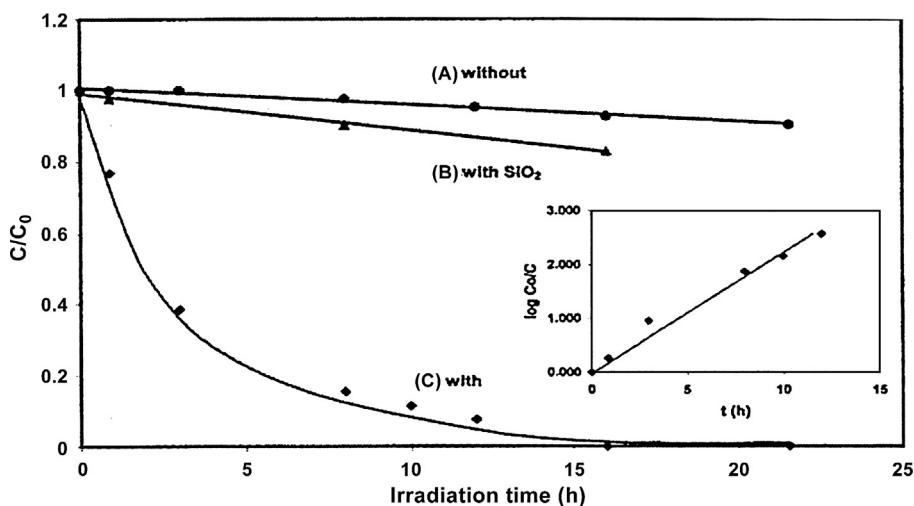


Fig. 11. Kinetics of decolorization (bleaching) of indigo carmine using visible light. Curve A: without any solid. Curve B: with photo-inactive SiO_2 , Curve C: with TiO_2 photocatalyst.

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3.3. Simultaneous visible and near-UV illumination

In yet another kinetic disguise, we consider the early data of Vautier et al. [10] who explored dye bleaching of a physical mixture of TiO_2 and indigo carmine powders. Their intimate mixture, prepared by slow evaporation of TiO_2 and solid indigo suspensions, should again exhibit a layer-by-layer intensity variation. Their observed apparent first order kinetic behavior, shown in Fig. 11 would be consistent with a zero order, multi-layer conversion disguised as first order by the layer-by-layer intensity variation with depth into the dried powder-dye mixture.

Vautier et al. [10] used a multi-wavelength lamp which could allow for photosensitized and/or photocatalyzed conversions of dyes, as represented in Fig. 6. This pathway may occur also under solar illumination. Thus, it is important, in using dyes as tests of (nUV/UVA) photocatalyst activity in a solar environment (paver stones, external window glass, etc.), to avoid use of a source containing sub-bandgap photons.

If, for a given dye, photosensitized (PS) conversion occurs and is the dominant process vs. solar photocatalysis, then a dye assay to demonstrate continued PCO activity may be inappropriate: most organic environmental contaminants are not dyes, and would not be expected to show photosensitization, so use of a simultaneous PCO/PS test system would overestimate the continuing, residual activity of the photocatalyst under solar illumination. On the other hand, use of a field-portable near-UV source could provide a true measure of residual PCO activity.

Our new kinetic model of dye oxidation within porous photocatalysts will exhibit apparent kinetic orders higher than the intrinsic (true) values for both photocatalysis (Julson [1]) and Vautier et al. data [11] as well as photosensitization (data of Vinodgopal et al. [12], Nasr et al. [13] and Porada and Gade [14]). Our analyses have assumed a uniform deposit of reactant dye within a porous catalyst.

4. Limiting cases

The examples discussed here are asymptotic: the photocatalyst layer is modeled as either highly light absorbing or as weakly absorbing (dilute TiO_2 in non-absorbing SiO_2). "Real world" samples may exhibit intermediate levels of optical absorbance, hence, intermediate apparent reaction orders. By chance, literature examples are often weakly absorbing (e.g., Activ glass of PPG, TiO_2

Table 1
Apparent reaction order, n .

Kinetics observed Light intensity: TiO_2	Intrinsic uniform (optically thin or non-porous)	Disguised non-uniform (optically thick and porous)
Dye coverage		
Low (sub-monolayer)	1	2
High (multi-layers)	0	1

thickness about 20 nm) or strongly absorbing (sol-gel films of thickness hundreds of nm), so literature data tend to fall into one of these two asymptotic areas, as shown by agreement of asymptotic model forms with the experimental examples cited in this article.

5. Summary

The observed dye oxidation reaction kinetics may be intrinsic or disguised, depending on the reactant-catalyst configuration. The analysis of this paper is summarized in Table 1, which shows that intrinsic chemical kinetic order is observed when the photocatalyst layer is optically thin (uniform illumination), regardless of whether the initial dye coverage is sub-monolayer ($n = 1$) or multi-layer ($n = 0$). When a non-uniform irradiance profile exists, as found in porous, optically dense catalyst films, the observed order of reaction increase by unity, thus an intrinsically first order reaction appears to be second order, and an intrinsically zero order reaction appears to be first order.

6. Conclusions

For photocatalyzed or photosensitized oxidation of uniform dye deposits on TiO_2 , the presence of uniform illumination on non-porous surfaces or non-uniform illumination of powder layers or meso-porous titania layers strongly influences the apparent reaction order observed, as summarized in Table 1 above.

Acknowledgement

Support from the State of North Carolina is appreciated.

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